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# Effects of partly-filled encapsulated phase change material on the performance enhancement of solar thermochemical reactor

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### A R T I C L E I N F O

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### ABSTRACT

Solar thermochemical reaction is an efficient way for hydrogen production. Due to cloud transients, solar thermochemical reactor endures low chemical conversion efficiency and deactivation of catalyst. To mitigate adverse effect of solar radiation fluctuation, in present paper, a solar thermochemical reactor design partly filled with encapsulated phase change material (EPCM) is proposed. Firstly, a twodimensional dynamic model of solar parabolic trough receiver reactors (SPTRR) partly filled with EPCM is established and validated against experimental data. Then, the steady-state performance of SPTRR under steady solar insolation is explored numerically, and the findings motivated us to create a novel multi-part filling pattern of EPCM designed to avoid high-temperature deactivation of catalyst. Furthermore, SPTRR's thermal and chemical behaviors under unsteady condition of solar radiation are analyzed. Finally, an optimal cascaded EPCM (regarding thermal properties) design is selected for the best overall dynamic performance of SPTRR. The results show that under the steady solar radiation, filled with EPCM in multi-part filling pattern, SPTRR can keep high methanol conversion efficiency (0.926) with large filling proportion (0.52) of EPCM, less usage of catalyst (reduced by 48% compared to allcatalyst case) and safe operation. And under the unsteady solar radiation, compared to SPTRR fully packed with catalyst, the delay response time and vibration amplitude of SPTRR with EPCM in 4-part filling pattern can be extended by 63.2% and damped by 48.7%, respectively. The comprehensive unsteady performance indicator of SPTRR with the optimal cascaded EPCM is 23.2% higher than that with non-cascaded EPCM.

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### 1. Introduction

Efficient utilization of solar resources is critical to the transition to a sustainable energy system energy globally (He et al., 2020; Li and Tao, 2017). As the clean alternative of fossil fuel, solar fuel, such as syngas or hydrogen produced by solar chemical reaction, has attracted considerable attention as they are storable and transportable (Zhao et al., 2018). There have been many solardriven method of hydrogen production, such as thermochemical reaction (Ishaq and Dincer, 2019), solar driven high-temperature electrolysis process (Yadav and Banerjee, 2018), photo bioreactors (Boran et al., 2010), photo-catalytic/electrochemical hydrogen production (Rather et al., 2018) and solar-driven supercritical water

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https://doi.org/10.1016/j.jclepro.2020.123169 0959-6526/© 2020 Published by Elsevier Ltd. gasification (Chen et al., 2019). Compared with traditional industrial procedure, hydrogen production through solar thermochemical reactions with concentrated solar radiation (E et al., 2019; Zuo et al., 2019), such as solar thermal water splitting, solar thermal cracking of methane (Zheng and Xu, 2018) and solar methanol steam reforming (Cheng et al., 2019b), has been shown to be potentially effective in commercial-scale operations and environmentally benign.

Solar thermochemical reactions can be roughly divided into two groups according to the operational temperature range of the reactions (Ma et al., 2020): high-temperature process (above 800 °C) and middle-and-low temperature process (below 500 °C). Usually, high temperature solar thermochemical reactions, such as water splitting cycle (Muhich et al., 2016), steam and CO<sub>2</sub> reforming of methane (Ishaq and Dincer, 2019), are operated above 800 °C in order to achieve high reaction rates and conversion efficiencies. For example, Chueh, Haile and Steinfeld et al. (Chueh et al., 2011)





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utilized the oxygen capture and release capability of cerium oxide and in a solar cavity-receiver reactor above 1500 °C to decompose CO<sub>2</sub> and H<sub>2</sub>O into CO and H<sub>2</sub>. Yu and Lu et al. (Yu et al., 2017) numerically and experimentally investigated the methane reforming process with CO<sub>2</sub> in a solar tubular and semi-cavity reactor. Their results showed that the maximum temperature of the reactor could reach above 1400 °C, and the thermochemical storage efficiency and total energy efficiency could reach 19.7% and 28.9%, respectively. However, high operational temperature may reduce the system thermal efficiency due to heat loss and optical loss, and also complicate the design and fabrication of the system (Liu et al., 2016). By contrast, middle-and-low temperature solar thermochemical reactions are often operated within the temperature range of 150-300 °C, which shows a great potential for practical applications (Cheng et al., 2019a). One of the most promising middle-and-low temperature chemical reactions is methanol steam reforming reaction, with several advantages such that methanol is producible from biomass, usually in liquid state at ambient condition for easy transportation and operation, and possesses relatively high H/C ratio, low reforming temperature (200–300 °C), which makes methanol steam reforming reaction a good hydrogen source (Iulianelli et al., 2014).

However, due to the transient nature of solar radiation, solar thermochemical reactor may endure unstable temperature fluctuation which may lower the chemical conversion efficiency (Rowe et al., 2018), cause the inactivation of catalyst and lead to unpredictable system shut down (Petrasch et al., 2009). Compared with concentrated solar power plant, the thermal management of solar fuel producing process is particularly challenging, because of its narrow working temperature and complex nonlinear characteristics of chemical reactions. Many researchers have focused on strategies to regulate the performance of chemical reactor during the solar radiation transients. Typically, there are two different types of methods to alleviate the adverse effect of unsteady solar radiation on solar chemical reactor: active control strategy (Liu et al., 2019) and passive thermal management.

In active control strategies, the reactant flow rate (Saade et al., 2014) or aperture (Najafabadi and Ozalp, 2018) of solar thermochemical reactors are often adjusted according to the dynamic solar radiation to maintain continuous high-performance operation. In order to deal with the variation of solar radiation caused by presence of cloud, Saade and Clough et al. (Saade et al., 2014) used model predictive controller to manipulate the flows rates into the solar chemical reactor. Their results showed that model predictive controller can minimize the effect of disturbance, which shows better control performance than multi-loop feedback strategy. Although model predictive control has better control accuracy than feedback control, the uncertainty in solar radiation forecast can negate the benefits from predictive control (Rowe et al., 2018). Meanwhile, the performance of temperature control is limited by locations of inserted thermocouples, which may not be distributed widely enough to detect each hot or cold spot (Odunsi et al., 2016). In addition, control precision and robustness are difficult to guarantee in the operations.

Passive thermal management by adding phase change material (PCM), which absorbs and releases large amount of latent heat at constant temperature (Ma et al., 2017; Yuan et al., 2019), can be an effective way for thermal regulation in solar thermochemical reactor. PCM has been widely applied in precise thermal management of battery systems (Zhang et al., 2018), buildings (Lamnatou et al., 2018), electric device (Manikandan et al., 2019) and electric vehicle (Hamut et al., 2014) to avoid the sudden change of temperature. Zhao and Rao et al. (Zhao et al., 2017) used paraffin as PCM for the thermal management of a cylindrical power battery. Their experimental results revealed that with PCM and heat pipe, the

maximum temperature of the battery cluster can be maintained below 50 °C for longer period of time than the air-based case. Qiao and Kong et al. (Qiao et al., 2020) conducted an experiment to explore the energy efficiency of active solar heating wall coupled with phase change material. Their experimental results showed that keep an indoor temperature of 25.52 °C and high cost effectiveness of 15.27, which are both higher than those of reference without PCM. However, few studies have been focused on the passive thermal management of solar thermochemical reactor using PCM. Pattison et al. (Pattison and Baldea, 2013) proposed a PCM-enhanced micro-channel chemical reactor for auto-thermal methane-steam reforming reactor, in which PCM is confined into a layer between the reactor plates, to mitigate the potential temperature excursion. The result showed that the proposed reactor and related control strategy can mitigate the disturbance of temperature well. In another design, Hatamachi and Gokon et al. (Gokon et al., 2008; Hatamachi et al., 2006) proposed a "doublewall" reactor for CO<sub>2</sub> reforming of methane (running over 700 °C) by filling phase change material into the shell side of solar tubular reformers. In their experiment, Na<sub>2</sub>CO<sub>3</sub> is adopted as PCM and MgO is mixed with Na<sub>2</sub>CO<sub>3</sub> to improve the thermal conductivity. Their experimental results demonstrated that adding PCM can benefit alleviation of chemical conversion decrease in the cooling mode of solar reactor, and showed the potential for solar chemical process under fluctuation of insolation. Furthermore, in chemical industry, the temperature stabilization of Fischer Tropsch reactor filled with the homogeneously-blend mixture of encapsulated phase change material (EPCM) and catalyst was investigated by O. Odunsi et al. (2016) using a steady-state model. They concluded that the distribution of catalyst temperature and chemical rate can be adjusted by filling EPCM at the steady state.

The literature review above indicates that PCM can prevent industrial thermochemical reactors, which are often exothermic (i.e., releasing heat to external environment), from overheating. Different from industrial thermochemical reactors, the solar thermal chemical reactor with methanol steam reforming reaction is endothermic and needs to absorb solar energy to support the chemical reaction. And the solar thermochemical reactor faces the cloudy transients and needs to avoid the chemical performance variation. Few studies have focused on thermal management of solar chemical reactor with PCM. In our prior work (Ma et al., 2018), PCM is added into thermochemical reactor in bulk to make it easy to fabricate, but the heat storing/releasing rate of PCM is limited due to its low thermal conductivity (Li et al., 2019). Thus more efficient way of incorporating PCM should be explored to achieve a better performance of solar thermochemical reactor. Meanwhile, the commonly used catalyst of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> pellet (Peppley et al., 1999) for methanol steam reforming reaction requires operational temperature below 573 K (300 °C) to avoid deactivation which limits the adding amount and position of PCM. Therefore, different from "double-wall" reactor where PCM is filled in annular space (Gokon et al., 2008; Hatamachi et al., 2006) or tubular reactor where catalyst is homogeneously mixed with EPCM (Odunsi et al., 2016), we propose a solar thermochemical reactor design for solar methanol steam reforming reaction partly filled with EPCM, which has several advantages such as high heat transfer area, high filling proportion of EPCM and safe operation. The novelty of this paper is (1) proposing a novel solar thermochemical reactor design partly filled with encapsulated phase change material, (2) steady and dynamic performance investigation of solar thermochemical reactor, (3) optimal cascaded combination of practical phase change material for solar methanol steam reforming reaction.

This paper is organized as follows. Firstly, a two-dimensional dynamic model of SPTRR partly filled with EPCM is established and validated with other's experimental data. Then, the steadystate performance of SPTRR partly filled with EPCM in 1-part filling pattern is analyzed and the effect of EPCM's filling proportion is investigated. Then, to avoid the overheating of catalyst caused by high filling proportion of EPCM filled in 1-part filling pattern, multipart filling pattern of EPCM is proposed and its steady performance is analyzed. Afterwards, dynamic thermal and chemical behaviors of SPTRR all filled with catalyst (i.e., without EPCM), partly filled with EPCM in different filling patterns under unsteady conditions of solar radiation are compared. Finally, in order to further improve the unsteady performance of SPTRR with the arrangement of different EPCM, sensitivity of EPCM's thermophysical properties on solar chemical reactor is discussed and optimal cascaded EPCMs is determined for the best comprehensive unsteady performance of SPTRR.

### 2. Model

### 2.1. Physical model

The structure of solar parabolic trough receiver reactor (SPTRR) partly filled with EPCM for methanol steam reforming reaction is illustrated in Fig. 1, which is mainly composed of 3 components: receiver tube, packed EPCM bed and packed catalyst bed. In present paper, LS2 solar parabolic trough receiver (Dudley et al., 1994), which is widely used in trough concentrated solar power plant, is employed to collect solar radiation and generate heat on the surface of a receiver tube for chemical reactions.

EPCM and catalyst are packed in different positions of SPTRR and separated by perforated plate, instead of mixed up like ref (Odunsi et al., 2016), to avoid the local hot or cold point caused by the non-uniform mixture of EPCM, which may lead to the failure of catalyst (Zhang et al., 2010). Also, the separately filling method of EPCM is easy for separation of catalyst and EPCM for future reuse. During the solar thermochemical reaction, solar radiation is projected on the outer surface of receiver, and then heat is transferred to EPCM and catalyst. After flowing into solar chemical reactor from inlet, reactants are heated in EPCM part at first and then flows into catalyst part, and reactions occur on the surface of catalyst. Finally, reactants and reaction product flow out of the reactor from outlet. The structural parameters of SPTRR are listed in Table 1. The tube is made of stainless steel 310 S. The density, specific heat and thermal conductivity of 310 S is 8 g cm<sup>-3</sup>, 500 J kg<sup>-1</sup>·K<sup>-1</sup> and 14.2 W m<sup>-1</sup>·K<sup>-1</sup>, respectively.

In SPTRR, Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> pellet (Peppley et al., 1999) is packed as

catalyst and Sn@SiO<sub>2</sub>, in which Sn is PCM and SiO<sub>2</sub> is the shell material of EPCM, is selected as EPCM (Zhang et al., 2010), due to Sn's proper melting point (505 K), high thermal conductivity and large latent heat. The thermophysical properties of catalyst and EPCM are shown in Table 1.

As indicated in reference (Wang et al., 2014), the influence of solar radiation distribution on the outer surface of solar chemical reactor is negligible. Meanwhile, the distribution uniformity of solar radiation can be greatly improved through some methods (He et al., 2018), such as adding secondary reflector (Gee and Winston, 2001), variable focus parabolic trough (Tsai and Lin, 2012) or adjusting aiming strategy (Qiu et al., 2017; Wang, K. et al., 2017). Thus, it is reasonable to assume that the solar radiation's distribution on the chemical reactor is uniform in the present paper. In addition, some assumptions are made to develop the mathematical model of SPTRR:

- (1) The inlet mass flow rate and temperature of reactor are constant.
- (2) The gas of reactant (CH<sub>3</sub>OH and H<sub>2</sub>O) and reaction production can be treated as ideal gas.
- (3) The packed catalyst bed is treated as isotropic porous media.
- (4) The fluid phase and solid phase are in local thermal equilibrium (Odunsi et al., 2016).
- (5) The EPCM and catalyst have the same size. And the porosities of packed catalyst and EPCM bed are equal (Nie et al., 2013).

### 2.2. Governing equation

The computational domain of a SPTRR partly filled with EPCM is shown in Fig. 2, which consists of packed EPCM bed, packed catalyst bed and outer tube, as illustrated in physical model of SPTRR in Fig. 1.

### 2.2.1. Packed EPCM bed region

The fluid flow in the packed EPCM bed is turbulent. The standard k-e turbulent model is adopted in present paper due to its robustness, economy and reasonable accuracy for a wide range of turbulent flows. Governing equations including continuity equation, momentum equation and energy conversation equation can be expressed as follows.

The continuity equation:



Fig. 1. Physical model structure of SPTRR partly filled with EPCM.

### Table 1

Structural parameters of solar chemical reactor (Harold et al., 2003) and thermophysical properties of catalyst and EPCM.

Parameter	Value
Structural parameters of solar chemical reactor	
Inner diameter of reactor tube <i>D<sub>i</sub></i> /m	0.066
Outer diameter of reactor tube $D_{o}/m$	0.07
Length of reactor tube L <sub>tube</sub> /m	5
Inlet molar ratio of H <sub>2</sub> O/CH <sub>3</sub> OH	1.1
Thermophysical properties of catalyst and EPCM	
Density of catalyst and EPCM $ ho_{\rm cat}$ and $ ho_{\rm EPCM}$ /kg·m <sup>-3</sup>	1300, 7184
Specific heat of catalyst and EPCM $c_{p,cat}$ and $c_{p,EPCM}$ /J·kg <sup>-1</sup> K <sup>-1</sup>	542, 244
Thermal conductivity of catalyst and EPCM $\lambda_{cat}$ and $\lambda_{p,EPCM}$ /W·m <sup>-1</sup> ·K <sup>-1</sup>	20, 67
Porosity of packed catalyst and EPCM bed $e_{cat}$ and $e_{EPCM}$	0.4, 0.4
Melting temperature of EPCM T <sub>m</sub> /K	505
Latent heat of EPCM $L_{\text{EPCM}}/\text{J}\cdot\text{kg}^{-1}$	60500



Fig. 2. Computational domain of solar chemical reactor partly filled with EPCM.

$$\frac{\partial(\varepsilon_{\text{EPCM}}\rho)}{\partial t} + \nabla \cdot (\varepsilon_{\text{EPCM}}\rho \,\overrightarrow{u}) = 0 \tag{1}$$

where  $\varepsilon_{\text{EPCM}}$  is the porosity of packed catalyst bed,  $\rho$  is the density of flow fluid,  $\vec{u}$  is the physical velocity of mixture fluid.

The momentum equation is expressed as:

$$\frac{\partial(\varepsilon_{\rm EPCM}\rho\,u\,)}{\partial t} + \nabla \cdot (\varepsilon_{\rm EPCM}\rho\,\overrightarrow{u}\,\overrightarrow{u}) = -\varepsilon_{\rm EPCM}\nabla p + \nabla \cdot \left[\varepsilon_{\rm EPCM}(\mu_{\rm t}+\mu)\left(\frac{\partial u_i}{\partial x_j}+\frac{\partial u_j}{\partial x_i}\right) - \frac{2}{3}\varepsilon_{\rm EPCM}(\mu_{\rm t}+\mu)\delta_{ij}\nabla \cdot \overrightarrow{u}\right] + \overrightarrow{S}_i$$
(2)

where  $\mu_t$  and  $\mu$  are, respectively, the turbulent and dynamic viscosity of flow fluid,  $\vec{S}_i$  is source term. The dynamic viscosity  $\mu$  can be expressed as (Hsueh et al., 2011):

$$\mu = \sum_{i} \frac{M_{i}\mu_{i}}{\sum_{j} M_{j}\varphi_{ij}} \tag{3}$$

$$\varphi_{ij} = \sum_{i} \left[ 1 + \left(\frac{\mu_i}{\mu_j}\right)^{\frac{1}{2}} \left(\frac{M_{w,j}}{M_{w,i}}\right) \right]^2 / \left[ 8 \left(1 + \frac{M_{w,j}}{M_{w,i}}\right) \right]^{\frac{1}{2}}$$
(4)

where  $M_i$  and  $M_{w,j}$  present the mole fraction and molar mass of specie *i*, respectively.

Source term  $\vec{S}_i$  can be calculated by Eq. (5).

$$\vec{S}_{i} = -\left(\varepsilon_{\text{EPCM}}^{2} \frac{\mu + \mu_{\text{t}}}{k_{\text{EPCM}}} \vec{u} + \frac{1}{2} \varepsilon_{\text{EPCM}}^{3} \beta \rho |\vec{u}| \vec{u}\right)$$
(5)

where the permeability  $k_{\text{EPCM}}$  and loss coefficient of resistance  $\beta$  are given by the Ergun equation (Ergun, 1952).

$$k_{EPCM} = d_{EPCM}^2 \varepsilon_{EPCM}^3 \left/ \left[ 150(1 - \varepsilon_{EPCM})^2 \right] \right.$$
(6)

$$\beta = 3.5(1 - \varepsilon_{EPCM}) \left/ \left( d_{EPCM} \varepsilon_{EPCM}^3 \right) \right.$$
(7)

where  $d_{\text{EPCM}}$  is the average diameter of EPCM and can be calculated by Eq. (8) (Zheng et al., 2015).

$$\varepsilon_{\text{EPCM}} = 0.375 + \frac{0.34d_{\text{EPCM}}}{D_{\text{i}}} \tag{8}$$

where  $D_i$  is the inner diameter of reactor tube. *k* (turbulence kinetic energy) equation:

$$\frac{\partial(\rho k)}{\partial t} + \nabla \cdot (\rho \,\overrightarrow{u} \,k) = \nabla \cdot \left[ \left( \mu + \frac{\mu_{t}}{\sigma_{k}} \right) \nabla k \right] + G_{k} - \rho \varepsilon \tag{9}$$

 $\varepsilon$  (turbulence kinetic energy dissipation rate) equation:

$$\nabla \cdot (\rho \overrightarrow{u} \varepsilon) = \nabla \cdot \left[ \left( \mu + \frac{\mu_{t}}{\sigma_{\varepsilon}} \right) \nabla \varepsilon \right] + \frac{\varepsilon}{k} (c_{1}G_{k} - c_{2}\rho\varepsilon)$$
(10)

where  $\sigma_k$  and  $\sigma_{\varepsilon}$  are, respectively, the Prandtl number of k and  $\varepsilon$ ,  $G_k$  presents the generation of turbulence kinetic energy caused by gradient of mean temperature,  $c_1$  and  $c_2$  are constants.  $\mu_t$  and  $G_k$  can be obtained by Eq. (11) and Eq. (12) respectively.

$$\mu_{\rm t} = c_{\mu} \rho \frac{k^2}{\varepsilon} \tag{11}$$

$$G_k = \mu_t \frac{\partial u_i}{\partial x_j} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)$$
(12)

where  $c_{\mu}$  is a constant. The standard value of constants in *k* equation and  $\varepsilon$  equation are:  $c_{\mu} = 0.09$ ,  $c_1 = 1.44$ ,  $c_2 = 1.92$ ,  $\sigma_k = 1.0$ ,

 $\sigma_{\varepsilon} = 1.3.$ 

The "effective heat capacity method" is employed to calculate the specific heat of EPCM during phase transition (Odunsi et al., 2016), which is shown in Eq. (13)

$$c_{p,\text{EPCM,eff}} = \begin{cases} c_{p,\text{EPCM}}, & T < T_{\text{m}} - \frac{\Delta T}{2} \\ c_{p,\text{EPCM}} + \frac{L_{\text{EPCM}}}{\Delta T}, & T_{\text{m}} - \frac{\Delta T}{2} \le T < T_{\text{m}} + \frac{\Delta T}{2} \\ c_{p,\text{EPCM}}, & T \ge T_{\text{m}} + \frac{\Delta T}{2} \end{cases}$$
(13)

where  $\Delta T$  is set to 2 K in this study (Odunsi et al., 2016).

The energy conservation equation for the packed EPCM region can be formulated by

$$\frac{\partial \left[ \varepsilon_{\text{PECM}} \rho_{f} c_{p,f} T + (1 - \varepsilon_{\text{EPCM}}) \rho_{\text{EPCM}} c_{p,\text{EPCM},\text{eff}} T \right]}{\partial t} + \nabla \cdot \left( \rho_{f} c_{p,f} \overrightarrow{u} T \right) = \nabla \cdot \left( \lambda_{\text{eff}} \nabla T \right)$$
(14)

where the effective thermal conductivity of packed region  $\lambda_{\text{eff}}$ , thermal conductivity of fluid mixture  $\lambda_{\text{f}}$ , and specific heat of fluid mixture  $c_{p,\text{f}}$  can be obtained by Eq.15–17.

$$\lambda_{\rm eff} = \varepsilon_{\rm cat} \lambda_{\rm f} + (1 - \varepsilon_{\rm cat}) \lambda_{\rm cat} \tag{16}$$

$$\lambda_{\rm f} = \sum_{i} \frac{M_i \lambda_i}{\sum_j M_j \varphi_{ij}} \tag{15}$$

$$c_{p,f} = \sum_{i} m_i c_{p,i} \tag{17}$$

### 2.2.2. Packed catalyst bed region

Governing equations of packed catalyst bed region including continuity equation, momentum equation, k-e equation, specie equation and energy conversation equation can be expressed as follows.

The continuity, momentum, and k- $\varepsilon$  equations of packed catalyst bed region are same with those of packed EPCM bed region.

The species conversation equation for each specie *i* can be expressed as:

$$\frac{\partial(\rho m_i)}{\partial t} + \nabla \cdot (\rho \vec{u} m_i) = \nabla \cdot \left[ \left( \rho D_{m,i} + \frac{\mu_t}{Sc_t} \right) \nabla m_i \right] + Y_i$$
(18)

where  $m_i$  and  $D_{m,i}$  are mass fraction and mass diffusivity of specie *i*, *Sc*<sub>t</sub> is the Schmidt number and set to be 0.7 (Zheng et al., 2015) in present study.  $Y_i$  is the source term for chemical reaction of specie *i* and can be expressed in Eq. (19).

$$Y_{i} = \begin{cases} M_{w,i} \sum_{r=1}^{N_{R}} \widehat{R}_{i,r} & \text{catalyst bed} \\ 0 & \text{EPCM bed} \end{cases}$$
(19)

where  $\hat{R}_{i,r}$  represents the generating/consuming rate of specie *i*.

Reactions occurring in the packed catalyst bed mainly include 3 chemical processes: methanol steam reforming reaction (MSR), methanol decomposition reaction (MDR), and water—gas shift reaction (WSR), which can be expressed as follows:

$$CH_3OH + H_2O \rightleftharpoons CO_2 + 3H_2 \tag{20}$$

$$CH_3OH \rightleftharpoons CO + 2H_2 \tag{21}$$

$$\mathrm{CO} + \mathrm{H}_2\mathrm{O} \rightleftharpoons \mathrm{CO}_2 + \mathrm{H}_2 \tag{22}$$

The comprehensive chemical kinetic model of methanol steam reforming model proposed by Peppley et al. (1999) is employed in this paper, which are shown in Eq. 23–25.

$$R_{\rm R} = \frac{k_{\rm R} K_{\rm CH3O_{(1)}} \frac{p_{\rm CH3OH}}{p_{\rm H_2}^{1/2}} \left( 1 - \frac{p_{\rm H_2}^3 p_{\rm CO_2}}{K_{\rm R} p_{\rm CH_3OH} p_{\rm H_2O}} \right) C_{\rm S1} C_{\rm S1a} S_{\rm g}}{\left( 1 + K_{\rm CH_3O_{(1)}} \frac{p_{\rm CH_3OH}}{p_{\rm H_2}^{1/2}} + K_{\rm HCOO} p_{\rm CO_2} p_{\rm H_2}^{1/2} + K_{\rm OH_{(1)}} \frac{p_{\rm H_2O}}{p_{\rm H_2}^{1/2}} \right) \left( 1 + K_{\rm H_{(1)}}^{1/2} p_{\rm H_2}^{1/2} \right)$$
(23)

$$R_{\rm D} = \frac{k_{\rm D} K_{\rm CH3O_{(2)}} \frac{p_{\rm CH_3OH}}{p_{\rm H_2}^{1/2}} \left(1 - \frac{p_{\rm H_2}^2 p_{\rm CO}}{K_{\rm D} p_{\rm CH_3OH}}\right) C_{\rm S2} C_{\rm S2a} S_{\rm g}}{\left(1 + K_{\rm CH_3O_{(2)}} \frac{p_{\rm CH_3OH}}{p_{\rm H_2}^{1/2}} + K_{\rm OH_{(2)}} \frac{p_{\rm H_2O}}{p_{\rm H_2}^{1/2}}\right) \left(1 + K_{\rm H_{(2)}}^{1/2} p_{\rm H_2}^{1/2}\right)}$$
(24)

$$R_{\rm W} = \frac{k_{\rm W} K_{\rm OH_{(1)}} \frac{p_{\rm CoP_{\rm CH3OH}}}{p_{\rm H_2}^{1/2}} \left(1 - \frac{p_{\rm H_2} p_{\rm Co_2}}{K_{\rm W} p_{\rm CoP_{\rm H_2}0}}\right) C_{\rm S1}^2 S_{\rm g}}{\left(1 + K_{\rm CH_3O_{(1)}} \frac{p_{\rm CH_3OH}}{p_{\rm H_2}^{1/2}} + K_{\rm HCOO} p_{\rm CO_2} p_{\rm H_2}^{1/2} + K_{\rm OH_{(1)}} \frac{p_{\rm H_2O}}{p_{\rm H_2}^{1/2}}\right)^2}$$
(25)

where  $R_R$ ,  $R_D$  and  $R_W$  represent the reaction rates of MSR, MDR and WSR, respectively;  $p_i$  is the partial pressure of specie *i*,  $C_{S1}$  and  $C_{S2}$  are the concentration of active site S1 and S2 on the catalyst surface, respectively;  $S_g$  presents the surface area of catalyst. These parameters are shown in Table A1.

Thus, the generating/consuming rate for each specie can be obtained through Eq. 26–30.

$$Y_{\rm CH_3OH} = -(R_{\rm R} + R_{\rm D})M_{\rm w, CH_3OH}$$

$$\tag{26}$$

$$Y_{\rm H_2O} = -(R_{\rm R} + R_{\rm W})M_{\rm w, H_2O} \tag{27}$$

$$Y_{\rm CO_2} = (R_{\rm R} + R_{\rm W}) M_{\rm w, CO_2} \tag{28}$$

$$Y_{\rm H_2} = (3R_{\rm R} + 2R_{\rm D} + R_{\rm W})M_{w,\rm H_2} \tag{29}$$

$$Y_{\rm CO} = (R_{\rm D} - R_{\rm W})M_{\rm w, CO}$$
 (30)

The energy conservative equation in the packed catalyst bed, based on the local thermal equilibrium, can be expressed as:

$$\frac{\partial \left[ \varepsilon_{\text{cat}} \rho_{\text{f}} c_{p,\text{f}} T + (1 - \varepsilon_{\text{cat}}) \rho_{\text{cat}} c_{p,\text{cat}} T \right]}{\partial t} + \nabla \cdot \left( \rho_{\text{f}} c_{p,\text{f}} \overrightarrow{u} T \right) = \nabla \cdot \left( \lambda_{\text{eff}} \nabla T \right)$$

$$+ S_{\text{t}}$$
(31)

where the energy source term  $S_t$  can be obtained by Eq. (32). In equations,  $h_{o,i}$  represents the enthalpy of formation for specie *i*, which is given in Table A2.

$$S_{t} = -\sum_{i} \left[ \left( h_{o,i} + \int_{T_{ref,i}}^{T} c_{p,i} dT \right) (Y_{i}) \right]$$
(32)

#### 2.2.3. Outer tube region

The energy conservative equation for heat conduction in the outer region can be expressed as:

$$\frac{\partial (\rho c_p T)_{\text{tube}}}{\partial t} = \nabla \cdot (\lambda_{\text{tube}} \nabla T)$$
(33)

where  $\lambda_{tube}$  is the thermal conductivity of tube.

### 2.3. Boundary and initial condition

As shown in the computational domain of Fig. 2, the boundary condition can be expressed as follows:

(1) For the packed catalyst and EPCM bed, the inlet and outlet boundary can be defined as:

Inlet: Flow velocity, temperature condition are constant and molar ratio of  $H_2O/CH_3OH$  is equal to be 1.1 to guarantee the high conversion of methanol.

$$u = u_{in}$$
,  $T = T_{in} = 423.15$  K,  $M_{H2O}/M_{CH3OH} = 1.1$ 

Outlet: constant pressure ( $p = p_{out} = 101325$  Pa).

(2) For the tube region, the end surfaces are adiabatic wall and can be expressed as:

 $\partial T/\partial x = 0.$ 

- (3) The axis of symmetry can be expressed as:  $\frac{\partial \vec{u}}{\partial r} = \frac{\partial T}{\partial r} = 0$
- (4) The interface between tube and packed catalyst/EPCM is coupled solid-fluid interface and can be defined as:  $\vec{u} = 0$ ,  $T_{cat} = T_{tube}$ .
- (5) In present paper, the direct normal irradiance (*DNI*) is taken as 600 W m<sup>-2</sup> constantly for steady-state SPTRR, and the average local concentration ratio (*LCR*) is set to 20 (Zheng et al., 2015), thus the heat flux on the outer surface of tube is 12000 W m<sup>-2</sup>.

The initial condition is set as follow. The temperature of tube of reactor, catalyst and EPCM are set to be the same at 473 K. In the reactor, the molar ratio of steam-and-methanol is set to be 1.1, the molar concentrator of H2, CO2 and CO are all set to be 0.

#### 2.4. Performance indicator of solar thermochemical reactor

The operation state of solar thermochemical reactors usually depends on the weather condition: solar thermochemical reactors are in steady state for sunny day with abundant and stable solar radiation, meanwhile in dynamic state for cloudy day with low and unsteady solar radiation. Thus, the steady-state and dynamic-state chemical performance of solar thermochemical reactor needs to be evaluated.

In present paper, the steady-state chemical performance of solar

thermochemical reactor under steady condition of solar radiation is evaluated by methanol conversion efficiency  $\eta_c$  which can be expressed as:

$$\eta_{\rm C} = \frac{m_{\rm CH_3OH,in} - m_{\rm CH_3OH,out}}{\dot{m}_{\rm CH_3OH,in}} \tag{34}$$

where the  $\dot{m}_{CH_3OH,in}$  and  $\dot{m}_{CH_3OH,out}$  are the mass flow rate of methanol at the inlet and outlet of reactor, respectively.  $\dot{m}_{CH_3OH}$  can be calculated by:

$$\dot{m}_{\rm CH_3OH} = \varepsilon_{\rm cat} A_{\rm cross} \rho u_x m_{\rm CH_3OH} \tag{35}$$

where  $A_{\text{cross}}$  is the crossing area of the solar thermochemical reactor.

For the unsteady condition of solar radiation, the solar radiation variation with time can roughly be divided into two different types: single step fluctuation and successive step fluctuation, which are shown in Fig. 3 (a) and (b) respectively, as indicated in Ref (Ma et al., 2018). Then, the delay response time  $\Delta t_{50,\eta_c}$  (Fridman, 2014) and relatively vibration amplitude  $\gamma_{\eta_c}$  of methanol conversion efficiency are adopted as evaluating indicators for the dynamic-state chemical performance of SPTRR under single and successive fluctuation of solar radiation respectively. The former one reflects the ability of SPTRR to retard the adverse effect of solar radiation's single fluctuation. And the latter one reveals the ability of SPTRR to keep stable under the successive fluctuation of solar radiation.

 $\Delta t_{50,\eta_c}$  is the delay time of SPTRR responses to the change of solar radiation and defined as the time SPTRR takes during which  $\eta_c$  changes by 50% of  $\Delta \eta_{c,total}$ . And  $\Delta \eta_{c,total}$  is the total absolute difference of stable methanol conversion efficiency before and after the change of solar radiation, which can be expressed as:

$$\Delta \eta_{\rm c,total} = \left| \eta_{\rm c,after} - \eta_{\rm c,before} \right| \tag{36}$$

 $\gamma_{\eta_c}$  is defined as the vibration amplitude of  $\eta_c$  over the timeaveraged  $\eta_c$  during one period of solar radiation's successive fluctuation when SPTRR reaches a repeatable state, and can be expressed as:

$$\gamma_{\eta_{\rm c}} = \frac{(\eta_{\rm c,max} - \eta_{\rm c,min})/2}{\eta_{\rm c,ave}} \tag{37}$$

where  $\eta_{c,max}$ ,  $\eta_{c,min}$  and  $\eta_{c,ave}$  present the highest, lowest and the average value of the methanol conversion efficiency of SPTRR during a cycle of solar radiation's fluctuation.

#### 2.5. Numerical method and model validation

The governing equations described above is solved by the Finite Volume Method (FVM). SIMPLE algorithm (Tao, 2001) is employed to achieve the coupling between velocity and pressure. The convective terms in momentum, species, and energy equations are discretized by second-order upwind scheme. Commercial Computational Fluid Dynamic (CFD) software Fluent is used to solve the governing equations. Calculation results from 4 different grid systems are compared to test the independence of grid, which are listed in Fig. 4 (a). From this figure, it can be seen that the difference of calculated methanol conversion efficiency between the gird system of  $5000(x) \times 36(r)$  and  $10000(x) \times 72(r)$  are negligible, indicating that the grid system of  $5000(x) \times 36(r)$  is adequate for simulating the heat transfer and chemical reaction in this solar chemical reactor, and will be adopted in the following simulations. As for the time-step independence test, simulation results of



Fig. 3. Illustration of two different typical solar radiation fluctuations.



Fig. 4. Grid and time-step independence test.



**Fig. 5.** Methanol conversion efficiency comparison between experiment (Peppley et al., 1999) and simulation.

different time steps ranging from 0.5 s to 5 s are examined. Fig. 4 (b) illustrates the result of time-step independence test with 4 different time steps. It can be seen that the variation curves of methanol conversion efficiency with time for time step of 1s and 2s is relatively close. As a result, the time step of 2 s is adopted in the simulations for adequate calculation accuracy and acceptable

computational cost.

For the model validation, calculation results in present paper are compared with the experimental data from Peppley (Peppley et al., 1999). In the experiment, the length and nominal diameter of reactor are 30 cm and 2.21 cm respectively. The Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst is packed in the reactor. During the experiment, the total pressure is 1.01 bar, and the molar ratio of water-to-methanol is 1.0. The numerical results and experimental data are compared at the temperature of 513 K and 533 K respectively. The comparison results are shown in Fig. 5, which shows that simulation results are in good agreement with experimental data for different operation temperature (513 K and 533 K) and mass flow rates of reactant and validates the accuracy of model established.

### 3. Results and discussion

### 3.1. Steady-state thermal and chemical performance of SPTRR partly filled with EPCM under steady condition of solar radiation

In this section, firstly, EPCM is packed in 1-part filling pattern and the performance of SPTRR with different filling proportions of EPCM in 1-part filling pattern are analyzed. Then, to avoid the overheat of catalyst caused high filling proportion of EPCM with 1part filling pattern, multi-filling pattern is proposed and the effect of EPCM filling pattern is discussed. In our simulations for the steady-state performance of SPTRR, the inlet mass flow rate of reactant is set to 0.01 kg s<sup>-1</sup>, and the heat flux on the outer surface of reactor is 12000 W m<sup>-2</sup>.





(b) Methanol consumption rate distribution along x axis

=0.

f=0.

f=0.





Fig. 6. Thermal and chemical performance of SPTRR with different filling proportions of EPCM in 1-part filling pattern.

# 3.1.1. Influence of EPCM's filling proportion in SPTRR with 1-part filling pattern

Fig. 6 (a) and (b), respectively, shows the variation of crosssectional averaged temperature and methanol consumption rate along flow direction of SPTRR for different filling proportions of EPCM in 1-part filling pattern. From Fig. 6 (a), it can be seen that when the filling proportion f = 0, namely SPTRR is fully packed with catalyst, the cross-sectional averaged temperature increases rapidly along the flow direction initially, and then the rate of increase in temperature is reduced due to the increasing chemical reaction rate of endothermic reaction (MSR and MDR) after x = 0.5 m, as can been observed in Fig. 6 (b). When x is larger than 2 m, with the consumption of reactants along the flow direction, the reaction rate decreases gradually and more solar energy is transferred into the sensible heat of fluid, thus the rate of increase in temperature is elevated again. In SPTRR partly filled with EPCM, namely f = 0.1, 0.2,0.3, when reactants flow into reactor, they are heated in the packed EPCM bed first, no reactions occur and the cross-sectional temperature of SPTRR increases linearly along the flow direction. When reactants flow into the packed catalyst region, the temperature drops rapidly because the endothermic chemical reactions (MSR and MD) occur at a relatively large reaction rate due to its high temperature and concentration of reactants as can be seen in Fig. 6 (b). With the consumption of reactants and decreasing of reaction rate along the flow direction, the temperature increases gradually again after reaching the lowest temperature. It can be found that as f increases, the highest temperature and consumption rate of CH<sub>3</sub>OH in SPTRR are both elevated which can benefit the volumeaverage reaction rate in the packed catalyst region.

Fig. 6 (c) shows the total thermal and chemical performance of

SPTRR with different filling proportions of EPCM in 1-part filling pattern. As can be seen from this figure, with the increasing of filling proportion *f*, the maximum temperature of catalyst is improved. When *f* increases from 0 to 0.3, the maximum temperature of catalyst is improved by 72.1 K and reaches as high as 625 K, which is beyond the allowable temperature limit for catalyst of 573 K (Wang, Y.J. et al., 2017). Thus, to ensure the long term and safe operation of SPTRR, the filling proportion of EPCM in reactor should not exceed 0.2.

As for the chemical performance, with the rising of f, which means less usage of catalyst in SPTRR, the methanol conversion efficiency and production rate of H<sub>2</sub> are almost unchanged, which can stay at 0.926 and 3.84 kg h<sup>-1</sup>, respectively. This phenomenon can be explained by the fact that higher filling proportion of EPCM can lead to the higher average catalyst temperature and faster volumetric-averaged reaction rate. And the production rate of CO is improved slightly with the increase of f, because the higher temperature of catalyst caused by higher f can accelerate chemical reaction rate of methanol decomposition reaction to produce more CO.

#### 3.1.2. Multi-part filling pattern of EPCM

As mentioned above, when EPCM only filled in the inlet part of SPTRR, the filling proportion of EPCM should not exceed 0.2 to avoid overheating of the catalyst. To further increase the thermal inertia (Odunsi et al., 2016) and improve the thermal stability of SPTRR under unsteady condition within the limited temperature range (lower than 573 K), the multi-part filling pattern of EPCM is proposed, such as 2-part, 3-part and 4-part filling pattern, which means that EPCM are separately packed into several different



(b) EPCM with 4-part filling pattern

Fig. 7. Illustration of SPTRR with 1-part and 4-part filling pattern of EPCM.

### Table 2Parameters of SPTRR with multi-part filling pattern of EPCM.

Length of each part (Total length $= 5 \text{ m}$ )	Filling pattern of EPCM			
	1 part	2 parts	3 parts	4 parts
No. 1	1.1 m (EPCM)	1.1 m (EPCM)	1.1 m (EPCM)	1.1 m (EPCM)
No. 2	3.9 m (Catalyst)	0.5 m (Catalyst)	0.5 m (Catalyst)	0.5 m (Catalyst)
No. 3	_	0.5 m (EPCM)	0.5 m (EPCM)	0.5 m (EPCM)
No. 4	_	2.9 m (Catalyst)	0.5 m (Catalyst)	0.5 m (Catalyst)
No. 5	_	_	0.5 m (EPCM)	0.5 m (EPCM)
No. 6	_	_	1.9 m (Catalyst)	0.5 m (Catalyst)
No. 7	_	_	_	0.5 m (EPCM)
No. 8	_	_	_	0.9 m (Catalyst)
Total filling proportion of EPCM	0.22	0.32	0.42	0.52

positions of SPTRR. Fig. 7 (a) and (b) illustrate SPTRR with 1-part and 4-part filling pattern of EPCM respectively. In SPTRR with 4part filling pattern of EPCM, EPCM are separately packed into 4 different parts of SPTRR, and packed EPCM beds are separated by the packed catalyst bed. Table 2 lists the structural parameters of different multi-part filling patterns to be investigated in present paper. For all of multi-part filling patterns, the first filling part of EPCM is at inlet area of SPTRR to improve the average temperature of catalyst and lengths of each part are selected to prevent temperature over-rising above the temperature limit of catalyst.

Fig. 8 (a) and (b) present the variation of cross-sectional averaged temperature and methanol consumption rate along fluid flow direction in SPTRR with different filling patterns of EPCM respectively. It is found in Fig. 8 (a) that in each EPCM-packed region, temperature increases linearly along the flow direction and drops rapidly in catalyst-packed region due to the endothermic reaction of MSR and MD. It can be noted that in the catalyst-packed region, the changing trends of temperature in catalyst-packed bed are almost the same for all of these different filling patterns of EPCM. From Fig. 8 (b), it can be seen that for SPTRR with 4-part filling pattern of SPTRR, the highest methanol consumption rate in each catalyst-packed region gradually decreases along the flow direction due to the decrease of reactants' concentration.

Fig. 8 (c) shows the total thermal and chemical performance of SPTRR with different filling patterns of EPCM. As the filling part number of EPCM in SPTRR increases, the filling proportion of EPCM and maximum temperature of catalyst are both improved. Compared to SPTRR fully filled with catalyst, when EPCM is filled in SPTRR with 4-part filling pattern, the filling proportion of EPCM largely increases to 0.52, meanwhile the maximum temperature of catalyst is 572.1 K which is still within the temperature limit of catalyst. As for the chemical performance, with the increasing of EPCM's filling parts, the methanol conversion efficiency keeps almost unchanged. When the filling pattern is changed from 'All-catalyst' to 4-part filling pattern, the methanol conversion efficiency of SPTRR is only reduced by about 1%, meanwhile the usage





(a) Averaged temperature distribution along x axis

(b) Methanol consumption rate distribution along x axis





Fig. 8. Thermal and chemical performance of SPTRRs with different filling patterns of EPCM.

of catalyst is reduced by 52% and thermal inertia is largely improved with high filling proportion of EPCM. As for the production of reaction, as the filling pattern of EPCM is adjusted from 1-part to 4-part pattern, the production rate of  $H_2$  is reduced by 1.8% and the production rate of CO is improved by 60.6%.

From the results above, it can be concluded that by packing EPCM in SPTRR in multi-part filling pattern, SPTRR can keep high methanol conversion efficiency with much less usage of catalyst, large mount (f = 0.52) of EPCM within the temperature limit.

## 3.2. Dynamic chemical performance of SPTRR partly filled with EPCM under unsteady condition of solar radiation

Impacted by the clouds transients, the solar radiation on the outer surface of SPTRR fluctuates greatly (Rowe et al., 2018). Thus, unsteady performance of SPTRR with partly filled with EPCM under different solar radiation's fluctuation needs to be investigated. In this section, the dynamic response of SPTRR with partly filled with EPCM to solar radiation's fluctuations are analyzed. As illustrated in Fig. 3, for the single step fluctuation of solar radiation, solar flux on the outer surface of SPTRR keeps constant at 12000 W m<sup>-2</sup> before 3 min, and then the solar flux suddenly drops to 0 after 3 min in simulations. Correspondingly, for the successive step fluctuation of solar radiation, the solar flux switches between 12000 and 0 W m<sup>-2</sup> for every 3 min, which is one of common time intervals for clouds transients as indicated in Ref (Ma et al., 2018).

## 3.2.1. Dynamic chemical behavior of SPTRR under single step fluctuation of solar radiation

In this section, the step fluctuation of solar radiation illustrated

in Fig. 3 (a) is projected on the outer surface of SPTRR. Fig. 9 (a) shows methanol conversion efficiency variation with time for different filling patterns of EPCM under single step fluctuation of solar radiation in Fig. 3 (a). As can be seen, after the solar radiation disappears after t = 3 min, methanol conversion efficiency of all SPTRRs drops at the beginning, and then the decreasing rate slows down gradually. For SPTRRs all packed with catalyst, methanol conversion efficiency gradually approaches a relatively low value which is almost equal to zero, while for SPTRRs partly filled with EPCM, methanol conversion efficiency drops to a relative high level and keeps stable for a long term firstly, and then decreases again to approach near zero. It can be found that as the filling parts of EPCM increases, the stable value in the decreasing process of methanol conversion efficiency is higher and the duration time of methanol conversion efficiency above a certain value (like 0.3) is extended. When the filling pattern of EPCM changes from all-catalyst to 4part filling pattern, the stable value of methanol conversion efficiency increases largely from near zero to 0.310, and the duration time of methanol conversion efficiency above 0.3 after the disappearance of solar radiation extends from 2.1 min to 15min. This phenomena is caused by the fact that as the filling pattern of EPCM changes from all-catalyst to 4-part pattern, the filling proportion of EPCM in SPTRR increases which can provide more latent heat for chemical reaction and can also improve the average temperature of catalyst after the disappearance of solar radiation to keep methanol conversion efficiency at a relatively higher value for longer time. Fig. 9 (b) illustrates  $\Delta t_{50,\eta_c}$  of SPTRR with different filling patterns of EPCM under single step fluctuation of solar radiation. As shown in Fig. 9 (b), when the filling pattern of EPCM is adjusted from allcatalyst to 4-part pattern, the delay response time of methanol



(a) Variation of methanol conversion efficiency with time (b) Delay response time of methanol conversion

efficiency,  $\Delta t_{50,n}$ 

Fig. 9. Methanol conversion efficiency variation with time and  $\Delta t_{50.n_e}$  for different filling patterns of EPCM under single step fluctuation of solar radiation.



Fig. 10. Methanol conversion efficiency variation with time and  $\gamma_{\eta_i}$  for different filling patterns of EPCM under successive fluctuation of solar radiation.

conversion efficiency increases from 1.27 min to 2.07 min, which is prolonged by 63.2% and the ability of SPTRR to retard the adverse of solar radiation's single fluctuation is improved.

## 3.2.2. Dynamic chemical behavior of SPTRR under successive fluctuation of solar radiation

In this section, the successive fluctuation of solar radiation illustrated in Fig. 3 (b) is projected on the outer surface of SPTRR. Fig. 10 (a) and (b) show instant and vibration amplitude of methanol conversion efficiency for different filling patterns of EPCM under successive fluctuation of solar radiation respectively. Clearly, from Fig. 10 (a) it can be seen that under the successive fluctuation of solar radiation, the methanol conversion efficiency of all SPTRRs vibrates with the fluctuation of solar radiation. And with the vibration process, vibration amplitudes of methanol conversion efficiency gradually decreases and finally reaches a repeatable fluctuation. It can be found that compared with all-catalyst, when SPTRR is full with EPCM in 4-part filling pattern, the lowest methanol conversion efficiency after SPTRR reaches a repeatable state is largely elevated from 0.213 to 0.314.

When the methanol conversion efficiency is relatively low (less than 0.3), there is too much impure substance in the reaction production which can lead the subsequent processes (separation

and purification, such as pressure swing adsorption (Liu et al., 2009)) to consume more energy and is very harmful to the economy of reaction system (Saade et al., 2014). Thus, in the present paper, the lowest limit of methanol conversion efficiency is set to 0.3, below which the production flows out from SPTRR is not to be further separated and purified and production of reactor is not considered in the calculation of methanol conversion efficiency. Fig. 10 (b) shows that with the increasing of EPCM's filling parts in SPTRR, the time-averaged methanol conversion efficiency is promoted. As for the stability of SPTRR under successive fluctuation of solar radiation, the relatively vibration amplitude of methanol conversion efficiency is damped gradually as the filling parts of EPCM increases due to the elevation of thermal inertial. For example, compared with SPTRR fully packed with catalyst, the time-averaged value and relatively vibration amplitude of methanol conversion efficiency in SPTRR with 4-part filling pattern of EPCM are respectively, improved by 16.5% and damped by 48.7%. Thus, it can be considered that compared to fully filled with catalyst, the time-averaged chemical performance and stability of SPTRR can be highly improved by filling EPCM with multi-part filling pattern. For the practical application, the reactor with 4part filling pattern of EPCM can replace the reactor fully packed with catalyst for less usage of catalyst and more stable



(a)  $\eta_c$  under single step fluctuation of solar radiation (b)  $\Delta t_{50,\eta_c}$  under single step fluctuation of solar radiation



(c) Chemical performance under successive fluctuations of solar radiation

Fig. 11. Dynamic chemical performance of SPTRR with different melting temperatures under fluctuation of solar radiation.

### performance.

### 3.3. Effect of EPCM's thermophysical properties on chemical performance of SPTRR

Thermophysical properties of EPCM, such as melting temperature and latent heat, are the key factors for chemical performance of SPTRR partly filled with EPCM, in this section, sensitivity of EPCM's thermo-physical properties on solar chemical reactor is discussed at first. And then to fully utilize the latent heat of EPCM and further improve the dynamic performance of SPTRR, the EPCM in SPTRR is arranged in a cascaded way (Yuan et al., 2018) and the best cascaded EPCMs is selected for the best comprehensive unsteady performance of SPTRR. In this section, effects of melting point and latent heat of EPCM are discussed. In simulations, EPCM is filled into SPTRR with 4-part filling pattern.

### 3.3.1. Effect of EPCM's melting temperature

Fig. 11 (a) shows the methanol conversion efficiency variation with time of SPTRR with different melting temperature under single step fluctuation of solar radiation. It can be seen that as the melting temperature of EPCM increases, methanol conversion efficiency SPTRR which can be kept stable in the decreasing process is higher, and the time duration of the stable methanol conversion efficiency is shorter. This is due to the fact that with increasing of EPCM's melting temperature, the initial melting proportion of EPCM is reduced and the latent heat stored by EPCM for thermochemical reaction is lesser. Another reason is that higher value of stable methanol conversion efficiency leads to larger heat releasing rate from EPCM to chemical reactions and the latent heat stored by EPCM is consumed faster, thus the duration of methanol conversion efficiency keeping stable is shorter. For example, when the melting temperature of EPCM is improved from 485 K to 525 K, the stable methanol conversion efficiency in the decreasing process is promoted from 0.206 to 0.437, which is improved by 107.4%, while the duration time is shortened by about half. Fig. 11 (b) shows  $\Delta t_{\eta_c,50}$  of SPTRR partly filled with EPCM for different melting temperature under single step fluctuation of solar radiation. Clearly, as the melting temperature of EPCM increases,  $\Delta t_{50,\eta_c}$  of SPTRR is gradually improved due to the elevated value of stable methanol conversion efficiency in decreasing process. For example, when melting temperature of EPCM increases from 485 K to 565 K,  $\Delta t_{50,\eta_c}$ is elevated from 2.03 min to 5.57 min, which is improved by 173.8%.

Fig. 11 (c) shows chemical performance of SPTRR partly filled with EPCM for different melting temperature under successive fluctuation of solar radiation. It can be seen that with the increasing of EPCM's melting temperature, the time-averaged methanol conversion efficiency increases at first and reaches the highest value of 0.483 at  $T_{\rm m} = 505$  K, and then decreases gradually. Also it can be noted that as  $T_{\rm m}$  increases,  $\gamma_{\eta_{\rm c}}$  decreases at first, reaches the lowest value of 0.367 at  $T_{\rm m} = 525$  K, and then rises again. This phenomena is caused by the fact that when  $T_{\rm m}$  is too low or too high, the proportion of EPCM that undergoes phase change during the one cycle of solar radiation's successive step fluctuation is small, and the effect of EPCM on alleviation of methanol conversion efficiency's fluctuation is attenuated. Thus, the melting temperature of EPCM



(a)  $\eta_c$  under single step fluctuation of solar radiation (b)  $\Delta t_{50,n}$  under single step fluctuation of solar radiation



(c) Chemical performance under successive fluctuations of solar radiation

Fig. 12. Dynamic chemical performance of SPTRR with different latent heat under fluctuation of solar radiation.

should be carefully considered and in this present paper, melting temperatures of 505 K and 525 K are recommended due to their high  $\eta_{c,ave}$  and low  $\gamma_{\eta_c}$  in the methanol steam reforming reaction.

### 3.3.2. Effect of EPCM's latent heat

In this section, the melting temperature of EPCM is set to 505 K and 545 K, respectively. The effect of EPCM's latent heat ranging from 0.5  $\times$  *L* to 3  $\times$  *L*, where *L* is equal to the latent heat of Sn, is analyzed.

Fig. 12 (a) shows the methanol conversion efficiency variation of SPTRR with different latent heats of EPCM under step fluctuation of solar radiation, separately. As can be seen in Fig. 12 (a), when the latent of EPCM increases from 0.5 L to 3 L, the duration of stable methanol conversion efficiency in the decreasing process is longer, due to the fact that more latent heat can be released from EPCM to chemical reaction with the increase of latent heat. Due to the fact that  $T_{\rm m}$  can greatly influence the stable value of methanol conversion efficiency in the decreasing process, the stable methanol conversion efficiency is 0.533 for  $T_{\rm m}=545$  K and 0.310 for  $T_{\rm m} = 505$  K, which are separately above and below the medium value  $\eta_{c \text{ medium}}$  (0.465) between the initial and final methanol conversion efficiency. This phenomena can lead to large difference of effect which latent heat has on  $\Delta t_{50,\eta_c}$  between melting temperature of 505 K and 545 K, which is illustrated in Fig. 12 (b). As can be seen, effect of latent heat on  $\Delta t_{50,\eta_c}$  varies based on  $T_{\rm m}$  of EPCM. As the latent heat of EPCM increases from 0.5 *L* to 3 *L*,  $\Delta t_{50,\eta_c}$ is prolonged greatly from 3.8 min to 9.0 min for  $T_{\rm m} = 545$  K, but it keeps almost unchanged for  $T_{\rm m} = 505$  K. Thus, it can be concluded

 $T_{\rm m}$  and latent heat of EPCM should be accordingly selected for the purpose of high  $\Delta t_{50,\eta_c}$ .

Fig. 12 (c) illustrates the chemical performance of SPTRR with different latent heat under successive fluctuation of solar radiation. As can be seen in this figure, when  $T_{\rm m}$  is equal to 505 K, with the increasing of latent heat from  $0.5 \times L$  to  $3 \times L$ ,  $\eta_{\rm c,ave}$  and  $\gamma_{\eta_c}$  are improved by 14.5% and reduced by 5.1% respectively, while for  $T_{\rm m} = 545$  K,  $\eta_{\rm c,ave}$  and  $\gamma_{\eta_c}$  are almost unchanged. This phenomena can be explained by the fact that when  $T_{\rm m}$  is relatively high (such as 545 K), after SPTRR reaches repeatable state, only small part of EPCM undergoes the melting-solidifying process, and then the latent heat is not the key factor influencing the chemical performance of SPTRR. When  $T_{\rm m}$  is lower (such as 505 K), the proportion of EPCM undergoing melting-solidifying process increases, and the improvement of latent heat can contribute to the increase of  $\eta_{\rm c,ave}$  and the decline of  $\gamma_n$ .

### 3.3.3. Performance improvement of SPTRR filled with cascaded EPCM

As discussed above, the performance of SPTRR is greatly affected by thermophysical properties of EPCM, which should be accordingly selected to achieve highly efficient and stable performance for SPTRR under unsteady condition of solar radiation. According to the fact that EPCM temperature varies depended on the position in SPTRR, thus in order to fully utilize the latent heat of EPCM (Yuan et al., 2018) and further improve the dynamic performance of SPTRR, EPCM is proposed to packed into SPTRR with cascaded way (Yuan et al., 2018), where EPCM with different melting temperature

Table 3	
Thermophysical properties (Jankowski and McCluskey, 2014) of available EPCM for methanol steam reforming read	tion.

No.	Name	$T_{\rm m}/{\rm K}$	$L/kJ \cdot kg^{-1}$	$ ho/{ m kg}\cdot{ m m}^{-3}$	$\lambda/W \cdot m^{-1} \cdot K^{-1}$	$c_p/\mathrm{kJ}\cdot\mathrm{kg}^{-1}\cdot\mathrm{K}^{-1}$
EPCM0	91Sn-9Zn (Indalloy 201)	472	71.2	7270	61	0.239
EPCM1	Sn	505	60.5	7280	73	0.257
EPCM2	Bi	544	53.3	9800	8.1	0.122

Table 4	4
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Arrangement of cascaded FPCM

 8				
Arrangement	Part 1	Part 2	Part 3	Part 4
case1	EPCM1	EPCM1	EPCM1	EPCM1
case2	EPCM0	EPCM1	EPCM1	EPCM1
case3	EPCM1	EPCM1	EPCM1	EPCM2
case4	EPCM1	EPCM1	EPCM2	EPCM2
case5	EPCM0	EPCM1	EPCM1	EPCM2

Annotation: EPCM 0, EPCM1 and EPCM2 present 91Sn-9Zn, Sn and Bi, respectively.

are arranged in series. Then the best cascaded arrangement of EPCM is selected considering the overall dynamic performance of EPCM.

Selected from the phase change material review (Jankowski and McCluskey, 2014), available EPCM occupying large latent heat, proper melting temperature (ranging from 423 K to 573 K) and high safety are listed in Table 3.

Table 4 shows different arrangements of cascaded EPCM, in which the melting temperature of EPCM increases or keeps unchanged along the flow direction to follow the increasing trend of SPTRR's temperature. Melting temperature distributions of different cascaded EPCM are illustrated in Fig. 13 (a). Case1 presents SPTRR partly fill with non-cascaded EPCM, and case2-5 are SPTRRs partly filled with cascaded EPCM.

Fig. 13 (b) and (c) present the unsteady chemical performance of SPTRR partly filled with cascaded EPCM under single step fluctuation and successive fluctuation of solar radiation, respectively. As can be seen in Fig. 13 (b), among arrangements of cascaded EPCM (case2 –case5), case4 shows longest  $\Delta t_{50,\eta_c}$ , which is improved by about 45.2% compared with non-cascaded (case1), Meanwhile, as is shown in Fig. 13 (c), when the solar radiation fluctuates successively, compared to the non-cascaded EPCMs (case1), the cascaded arrangement of EPCM has slight effect on the time-averaged  $\eta_c$ , but leads to higher  $\gamma_{\eta_c}$ . Take case4 as an example, which has highest  $\gamma_{\eta_c}$ among all cascaded cases, and  $\gamma_{\eta_c}$  of case 4 is expanded by 17.7% compared to non-cascaded (case1). This phenomena can be explained by the fact that, according to the result in Fig. 11 (b), EPCM with high melting temperature has adverse effect on the stability of SPTRR, and case4 has highest proportion of highmelting-temperature EPCM among all cases (case1-case5) which can lead to larger value of  $\gamma_{\eta_c}$  and worse stability. To comprehensively evaluate the chemical performance of

SPTRR under different unsteady conditions, comprehensive



(a) Melting temperature distribution



Fig. 13. Chemical performance of SPTRR partly filled with different cascaded EPCM under unsteady condition.



Fig. 14.  $\omega$  of SPTRR with different cascaded EPCM.

indictor of unsteady chemical performance  $\omega$  is proposed. The metric  $\omega$  involves not only the response time of SPTRR under single step fluctuation of solar radiation, but also the stability of SPTRR under successive fluctuation of solar radiation, which is defined as Eq. (38). And higher  $\omega$  reflects better unsteady performance of SPTRR.

$$\omega_{\eta_c} = \left(\frac{t_{50,\eta_c}}{t_{50,\eta_c,o}}\right) \left/ \left(\frac{\gamma_{\eta_c}}{\gamma_{\eta_c,o}}\right) \right. \tag{38}$$

where  $t_{50,\eta_c,o}$  and  $\gamma_{\eta_c,o}$  represent  $t_{50,\eta_c}$  and  $\gamma_{\eta_c}$  of SPTRR fully packed with catalyst.

Fig. 14 illustrates  $\omega$  of SPTRR with different cascaded EPCM. As can be seen in this figure, among these different arrangements of cascaded EPCM, case4 has the highest  $\omega$  of 3.40 and is improved by 23.2% compared to that of SPTRR with non-cascaded EPCM (case1). Also, it also should be noted that the comprehensive unsteady chemical performance indictor  $\omega$  of case 2 and case 5 (with cascaded EPCM) are lower than that of case 1 (without cascaded EPCM). Therefore, it can be concluded that the cascaded arrangement of EPCM has the potential to improve the compressive unsteady performance of SPTRR, and the arrangement of EPCM should be carefully decided. In present paper, the cascaded EPCM of case4 is recommended and can improve the unsteady performance of SPTRR at most. Thus, for the solar methanol steam reforming reactor, the cascaded combination of Sn-Sn-Bi-Bi EPCM should be applied in reactor to achieve high conversion efficiency and stable production of hydrogen.

### 4. Conclusion

In present paper, solar parabolic trough receiver reactor partly filled with encapsulated phase change material is proposed to alleviate the adverse of could transients on the thermal and chemical performance of solar thermochemical reactor. Firstly, a two-dimensional computational model is established and validated against experimental data. Then, the steady performance of SPTRR partly filled with EPCM is explored and the effect of EPCM's filling proportion is discussed. Then, to avoid the deactivation of catalyst caused by overheating with high filling proportion of EPCM in 1part filling pattern, multi-part filling pattern of EPCM is proposed. Furthermore, thermal and chemical behaviors of SPTRR all filled with catalyst and partly filled with EPCM under different unsteady conditions are compared. Finally, the sensitivity of EPCM's thermophysical properties on solar chemical reactor is analyzed, and optimal cascaded EPCMs is obtained for the best comprehensive performance of SPTRR. Compared with traditional industrial procedure, the solar-driven hydrogen production can greatly reduce the CO<sub>2</sub> emission and achieve the zero-carbon utilization of clean energy. The proposed solar thermochemical reactor with encapsulated phase change material can improve the chemical conversion efficiency and stability of hydrogen production, which is very beneficial to environment and sustainable development. To promote the practical application of reactor with partly filled encapsulated phase change material, the fabrication method of high-temperature encapsulated phase change material should be further explored. The actual performance of reactor under realistic solar radiation will be experimentally investigated for the future work. The salient findings are as follows:

- (1) When solar radiation is stable, as the filling proportion of EPCM in SPTRR with 1-part filling pattern increases, the steady-state chemical performance of SPTRR keeps at high level with less catalyst, and the maximum temperature of catalyst also increases. For example, when the filling proportion of EPCM in SPTRR increases from 0 to 0.3, with the decreasing usage of catalyst, the methanol conversion efficiency and production rate of H<sub>2</sub> are almost unchanged. This phenomena can be explained by the fact that higher filling proportion of EPCM can lead to the higher average catalyst temperature and faster volumetric-averaged reaction rate. However, the filling proportion of EPCM in 1-filling pattern should not exceed 0.2 to ensure the long and safe operation of SPTRR.
- (2) For the steady-state chemical performance, compared with 1-part filling pattern, when EPCM is filled into SPTRR with multi-part filling pattern as proposed in this paper, SPTRR can be filled with larger filling proportion (f = 0.52 for 4-part filling pattern) of EPCM and lesser catalyst (only 48% compared with SPTRR fully filled with catalyst for 4-part filling pattern) which still satisfies the requirement of catalyst temperature and keep high methanol conversion efficiency.
- (3) For the dynamic chemical performance, the delay response time and stability of SPTRR with EPCM in multi-part filling pattern under unsteady condition can be largely improved. When the filling method of EPCM is adjusted from allcatalyst to 4-part pattern, the delay response time and relatively vibration amplitude of methanol conversion efficiency under single and successive step fluctuation of solar radiation are, respectively, prolonged by 63.2% and damped by 48.7% which are beneficial for control of SPTRR and stable separation and purification process of reaction production.
- (4) The dynamic chemical performance of SPTRR is greatly affected by thermophysical properties of EPCM and the cascaded arrangement of EPCM has the potential to improve the compressive dynamic performance of SPTRR. The comprehensive unsteady performance indicator of SPTRR filled with the optimal cascaded EPCM is 23.2% higher than that of SPTRR with non-cascaded EPCM of Sn@SiO<sub>2</sub>.

### **CRediT authorship contribution statement**

**Zhao Ma:** Investigation, Methodology, Formal analysis, Validation, Writing - original draft, Software. **Ming-Jia Li:** Supervision, Project administration, Conceptualization, Writing - review & editing. **Ya-Ling He:** Project administration, Supervision, Conceptualization, Funding acquisition. **K. Max Zhang:** Writing - review & editing.

### **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A

total heat transfer rate, W Q universal gas constant, J·mol<sup>-1</sup>·K<sup>-1</sup> R reaction rate of methanol steam reforming reaction,  $R_{\rm R}$  $mol \cdot m^{-3} \cdot s^{-1}$ reaction rate of methanol decomposition reaction,  $R_{\rm D}$  $mol \cdot m^{-3} \cdot s^{-1}$ 

reaction rate of water shift reaction,  $mol \cdot m^{-3} \cdot s^{-1}$ R<sub>W</sub>

velocity vector, m · s<sup>-1</sup>  $\overrightarrow{u}$ 

### Greek symbols

β	inertial loss coefficient, m <sup>-1</sup>
$\gamma_{\eta_c}$	relatively vibration amplitude of methanol conversion
	efficiency
$\Delta t_{50,\eta_c}$	delay response time of methanol conversion efficiency, s
ε	turbulence kinetic energy dissipation rate, $m^2 \cdot s^{-3}$
$\varepsilon_{cat}$	porosity of packed catalyst bed
$\varepsilon_{\text{EPCM}}$	porosity of packed EPCM bed
$\eta_{c}$	methanol conversion efficiency

### Table A1

Parameters in chemical kinetic models of methanol steam reforming reaction (Harold et al., 2003; Peppley et al., 1999)

Parameters	Value	Parameters	Value
$\begin{array}{c} k_{\rm R}/m^2 \cdot {\rm s}^{-1} \cdot {\rm mol}^{-1} \\ k_{\rm D}/m^2 \cdot {\rm s}^{-1} \cdot {\rm mol}^{-1} \\ k_{\rm W}/m^2 \cdot {\rm s}^{-1} \cdot {\rm mol}^{-1} \\ K_{\rm CH30(1)} \\ K_{\rm CH30(2)} \\ K_{\rm HCOO} \\ K_{\rm OH(1)} \\ K_{\rm OH(2)} \end{array}$	$\begin{array}{l} 7.4 \times 10^{14} e^{-102800/(RT)} \\ 3.8 \times 10^{20} e^{-170000/(RT)} \\ 5.9 \times 10^{13} e^{-87600/(RT)} \\ e^{-41.8/R+20000/(RT)} \\ e^{30/R+20000/(RT)} \\ e^{179.2/R-100000/(RT)} \\ e^{-44.5/R+20000/(RT)} \\ e^{30/R+20000/(RT)} \end{array}$	$K_{H(1)}$ $K_{H(2)}$ $K_{R}$ $K_{D}$ $K_{W}$ $C_{s1},C_{s2}/mol \cdot m^{-2}$ $C_{s1a},C_{s2a}/mol \cdot m^{-2}$ $S_{g}/m^{2} \cdot kg^{-1}$	$\begin{array}{c} e^{-100.8/R+50000/(RT)}\\ e^{-46.2/R+50000/(RT)}\\ 10^{-3066/T+10.592}\\ 10^{-5139/T+12.621}\\ 10^{2073/T-2.029}\\ 7.5\times10^{-6}\\ 1.5\times10^{-5}\\ 50000 \end{array}$

λ

μ

 $\mu_{\rm t}$ 

<b>Table A2</b> Enthalpy of forma	ation for each s	specie (Poling	et al., 200	01)	
Species	CH₃OH	H <sub>2</sub> O	$H_2$	CO <sub>2</sub>	CO
$h_{o,i}/kJ \cdot mol^{-1}$	-200.94	-241.81	0	-393.51	-110.53

ρ	density, kg∙m <sup>-3</sup>
$\delta_{ii}$	Kronecker's delta

comprehensive unsteady performance indicator  $\omega_{\eta_c}$ 

thermal conductivity,  $W \cdot m^{-1} \cdot K^{-1}$ 

dynamic viscosity, Pa·s

turbulent viscosity, Pa·s

density, kg · m<sup>-3</sup>

### Nomenclature and units

Α	cross area
<i>c</i> <sub>p</sub>	specific heat, J·kg <sup>-1</sup> ·K <sup>-1</sup>
<i>d</i> <sub>cat</sub>	diameter of catalyst particles, m
D	diameter, m
f	filling proportion of EPCM
$h_0$	formation enthalpy, J∙mol <sup>-1</sup>
k <sub>cat</sub>	permeability of catalyst, m <sup>2</sup>
k	turbulence kinetic energy, $m^2 \cdot s^{-2}$
L	latent heat, J·kg <sup>-1</sup>
L <sub>tube</sub>	length of tube, m
ṁ	mass flow rate, kg $\cdot$ h $^{-1}$
m <sub>i</sub>	mass fraction of species <i>i</i>
$M_i$	mole fraction of species <i>i</i>
M <sub>w</sub> ,i	molecular weight of species <i>i</i> , kg·mol <sup>-1</sup>
п	molar flow rate, $mol \cdot s^{-1}$
$\widehat{R}_{ir}$	rates of creation and destruction of species <i>i</i> in the
•,•	reaction r, mol·m <sup><math>-3</math></sup> ·s <sup><math>-1</math></sup>
Sct	effective turbulent Schmidt number
t	time, s
Т	temperature, K
р	pressure, Pa

### Subscripts

ave	average
cat	catalyst
eff	effective
	fluid
	inner face
	species
C	outer face
5	solid
Abbreviati	ons
DNI	direct normal irradiance
EPCM	Encapsulated phase char

EPCM	Encapsulated phase change material
MD	methanol decomposition
MSR	methanol steam reforming
PCM	phase change material
SPTRR	solar parabolic trough receiver reactor
WFR	weight of catalyst/inlet methanol molar flow rat
WSR	water—gas shift reaction

### References

Boran, E., Ozgur, E., Der Burg, J.V., Yucel, M., Gunduz, U., Eroglu, I., 2010. Biological hydrogen production by Rhodobacter capsulatus in solar tubular photo bioreactor. J. Clean. Prod. 18, S29-S35.

Chen, J.W., Xu, W.W., Zuo, H.Y., Wu, X.M., E, J.Q., Wang, T.S., Zhang, F., Lu, N., 2019.

System development and environmental performance analysis of a solar-driven supercritical water gasification pilot plant for hydrogen production using life cycle assessment approach. Energy Convers. Manag. 184, 60–73.

- Cheng, Z.D., Men, J.J., Liu, S.C., He, Y.L., 2019a. Three-dimensional numerical study on a novel parabolic trough solar receiver-reactor of a locally-installed Kenics static mixer for efficient hydrogen production. Appl. Energy 250, 131–146.
- Cheng, Z.D., Men, J.J., Zhao, X.R., He, Y.L., Tao, Y.B., 2019b. A comprehensive study on parabolic trough solar receiver-reactors of methanol-steam reforming reaction for hydrogen production. Energy Convers. Manag. 186, 278-292.
- Chueh, W.C., Falter, C., Abbott, M., Scipio, D., Furler, P., Haile, S.M., Steinfeld, A., 2011. High-flux solar-driven thermochemical dissociation of CO<sub>2</sub> and H<sub>2</sub>O using nonstoichiometric ceria. Science 330 (12), 1797–1801.
- Dudley, V., Kolb, G., Sloan, M., Kearney, D., 1994. SEGS LS2 Solar Collector—Test Results. Report of Sandia National Laboratories. Report No. SANDIA94-1884.
- E, J.Q., Liu, G.L., Liu, T., Zhang, Z.Q., Zuo, H.Y., Hu, W.Y., Wei, K.X., 2019. Harmonic response analysis of a large dish solar thermal power generation system with wind-induced vibration. Sol. Energy 181, 116–129.
- Ergun, S., 1952. Fluid flow through packed columns. Chem. Eng. Prog. 48 (2), 89–94. Fridman, E., 2014. Introduction to Time-Delay Systems: Analysis and Control. Birkhäuser. Basel.
- Gee, R., Winston, R., 2001. A non-Imaging secondary reflector for parabolic trough concentrators. Report to NREL, Duke Solar Energy, Raleigh, NC.
- Gokon, N., Nakano, D., Inuta, S., Kodama, T., 2008. High-temperature carbonate/ MgO composite materials as thermal storage media for double-walled solar reformer tubes. Sol. Energy 82 (12), 1145–1153.
- reformer tubes. Sol. Energy 82 (12), 1145–1153. Hamut, H., Dincer, I., Naterer, G., 2014. Exergoenvironmental analysis of hybrid electric vehicle thermal management systems. J. Clean. Prod. 67, 187–196.
- Harold, M.P., Nair, B., Kolios, G., 2003. Hydrogen generation in a Pd membrane fuel processor: assessment of methanol-based reaction systems. Chem. Eng. Sci. 58 (12), 2551–2571.
- Hatamachi, T., Kodama, T., Isobe, Y., Nakano, D., Gokon, N., 2006. Double-walled reactor tube with molten salt thermal storage for solar tubular reformers. J. Solar Energy Eng. Trans. ASME 128 (2), 134–138.
  He, Y.L., Qiu, Y., Wang, K., Yuan, F., Wang, W.Q., Li, M.J., Guo, J.Q., 2020. Perspective of
- He, Y.L., Qiu, Y., Wang, K., Yuan, F., Wang, W.Q., Li, M.J., Guo, J.Q., 2020. Perspective of concentrating solar power. Energy 198, 117373.
- He, Y.L., Wang, K., Qiu, Y., Du, B.C., Liang, Q., Du, S., 2018. Review of the solar flux distribution in concentrated solar power: non-uniform features, challenges, and solutions. Appl. Therm. Eng. 230, 448–474.
- Hsueh, C.Y., Chu, H.S., Yan, W.M., Leu, G.C., Tsai, J.I., 2011. Three-dimensional analysis of a plate methanol steam micro-reformer and a methanol catalytic combustor with different flow channel designs. Int. J. Hydrogen Energy 36 (21), 13575–13586.
- Ishaq, H., Dincer, I., 2019. Analysis and optimization for energy, cost and carbon emission of a solar driven steam-autothermal hybrid methane reforming for hydrogen, ammonia and power production. J. Clean. Prod. 234, 242–257.
- Iulianelli, A., Ribeirinha, P., Mendes, A., Basile, A., 2014. Methanol steam reforming for hydrogen generation via conventional and membrane reactors: a review. Renew. Sustain. Energy Rev. 29, 355–368.
- Jankowski, N.R., McCluskey, F.P., 2014. A review of phase change materials for vehicle component thermal buffering. Appl. Energy 113, 1525–1561.
- Lamnatou, C., Motte, F., Notton, G., Chemisana, D., Cristofari, C., 2018. Building-integrated solar thermal system with/without phase change material: life cycle assessment based on ReCiPe, USEtox and Ecological footprint. J. Clean. Prod. 193, 672–683.
- Li, M.J., Li, M.J., He, Y.L., Tao, W.Q., 2019. A novel semi-empirical model on predicting the thermal conductivity of diathermic oil-based nanofluid for solar thermal application. Int. J. Heat Mass Tran. 138, 1002–1013.
- Li, M.J., Tao, W.Q., 2017. Review of methodologies and polices for evaluation of energy efficiency in high energy-consuming industry. Appl. Energy 187, 203–215.
- Liu, G., Liu, J., Jiaqiang, E., Li, Y., Zhang, Z., Chen, J., Zhao, X., Hu, W., 2019. Effects of different sizes and dispatch strategies of thermal energy storage on solar energy usage ability of solar thermal power plant. Appl. Therm. Eng. 156, 14–22.
- Liu, Q.B., Hong, H., Yuan, J.L., Jin, H.G., Cai, R.X., 2009. Experimental investigation of hydrogen production integrated methanol steam reforming with middletemperature solar thermal energy. Appl. Energy 86 (2), 155–162.
- Liu, Q.B., Wang, Y.J., Lei, J., Jin, H.G., 2016. Numerical investigation of the thermophysical characteristics of the mid-and-low temperature solar receiver/reactor for hydrogen production. Int. J. Heat Mass Tran. 97, 379–390.
- Ma, Z., Li, M.J., He, Y.L., Zhang, K.M., 2020. Performance analysis and optimization of solar thermochemical reactor by diluting catalyst with encapsulated phase change material. Appl. Energy 266, 114862.
- Ma, Z., Yang, W.W., Li, M.J., He, Y.L., 2018. High efficient solar parabolic trough receiver reactors combined with phase change material for thermochemical reactions. Appl. Energy 230, 769–783.
- Ma, Z., Yang, W.W., Yuan, F., Jin, B., He, Y.L., 2017. Investigation on the thermal performance of a high-temperature latent heat storage system. Appl. Therm. Eng, 122, 579–592.
- Manikandan, S., Selvam, C., Poddar, N., Pranjyal, K., Lamba, R., Kaushik, S., 2019. Thermal management of low concentrated photovoltaic module with phase change material. J. Clean. Prod. 219, 359–367.
- Muhich, C.L., Ehrhart, B.D., Al-Shankiti, I., Ward, B.J., Musgrave, C.B., Weimer, A.W.,

2016. A review and perspective of efficient hydrogen generation via solar thermal water splitting. Wiley Interdisciplinary Rev.: Energy Environ. 5 (3), 261–287.

- Najafabadi, H.A., Ozalp, N., 2018. Aperture size adjustment using model based adaptive control strategy to regulate temperature in a solar receiver. Sol. Energy 159, 20–36.
- Nie, Y., Witt, P.M., Agarwal, A., Biegler, L.T., 2013. Optimal active catalyst and inert distribution in catalytic packed bed reactors: ortho-xylene oxidation. Ind. Eng. Chem. Res. 52 (44), 15311–15320.
- Odunsi, A.O., O'Donovan, T.S., Reay, D.A., 2016. Temperature stabilisation in Fischer-Tropsch reactors using phase change material (PCM). Appl. Therm. Eng. 93, 1377–1393.
- Pattison, R.C., Baldea, M., 2013. A thermal-flywheel approach to distributed temperature control in microchannel reactors. AIChE J. 59 (6), 2051–2061.
- Peppley, B.A., Amphlett, J.C., Kearns, L.M., Mann, R.F., 1999. Methanol-steam reforming on Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts. Part 2. A comprehensive kinetic model. Appl. Cataly. A General 179 (1-2), 31-49.
- Petrasch, J., Osch, P., Steinfeld, A., 2009. Dynamics and control of solar thermochemical reactors. Chem. Eng. J. 145 (3), 362–370.
- Poling, B.E., Prausnitz, J.M., O'connell, J.P., 2001. The Properties of Gases and Liquids. Mcgraw-hill, New York.
- Qiao, X., Kong, X., Li, H., Wang, L., Long, H., 2020. Performance and optimization of a novel active solar heating wall coupled with phase change material. J. Clean. Prod. 250, 119470.
- Qiu, Y., Li, M.J., Wang, K., Liu, Z.B., Xue, X.D., 2017. Aiming strategy optimization for uniform flux distribution in the receiver of a linear Fresnel solar reflector using a multi-objective genetic algorithm. Appl. Energy 205, 1394–1407.
   Rather, R.A., Pooja, D., Kumar, P., Singh, S., Pal, B., 2018. Plasmonic stimulated
- Rather, R.A., Pooja, D., Kumar, P., Singh, S., Pal, B., 2018. Plasmonic stimulated photocatalytic/electrochemical hydrogen evolution from water by (001) faceted and bimetallic loaded titania nanosheets under sunlight irradiation. J. Clean. Prod. 175, 394–401.
- Rowe, S.C., Hischier, I., Palumbo, A.W., Chubukov, B.A., Wallace, M.A., Viger, R., Lewandowski, A., Clough, D.E., Weimer, A.W., 2018. Nowcasting, predictive control, and feedback control for temperature regulation in a novel hybrid solar-electric reactor for continuous solar-thermal chemical processing. Sol. Energy 174, 474–488.
- Saade, E., Clough, D.E., Weimer, A.W., 2014. Model predictive control of a solarthermal reactor. Sol. Energy 102, 31–44.
- Tao, W.Q., 2001. Numerical Heat Transfer. Xi'an Jiaotong University Press, Xi'an.
- Tsai, C.Y., Lin, P.D., 2012. Optimized variable-focus-parabolic-trough reflector for solar thermal concentrator system. Sol. Energy 86 (5), 1164–1172.
- Wang, K., He, Y.L., Li, P., Li, M.J., Tao, W.Q., 2017. Multi-objective optimization of the solar absorptivity distribution inside a cavity solar receiver for solar power towers. Sol. Energy 158, 247–258.
- Wang, Y.J., Liu, Q.B., Lei, J., Jin, H.G., 2014. A three-dimensional simulation of a parabolic trough solar collector system using molten salt as heat transfer fluid. Appl. Therm. Eng. 70 (1), 462–476.
- Wang, Y.J., Liu, Q.B., Sun, J., Lei, J., Ju, Y., Jin, H.G., 2017. A new solar receiver/reactor structure for hydrogen production. Energy Convers. Manag. 133, 118–126.
- Yadav, D., Banerjee, R., 2018. Economic assessment of hydrogen production from solar driven high-temperature steam electrolysis process. J. Clean. Prod. 183, 1131–1155.
- Yu, T., Yuan, Q.Y., Lu, J.F., Ding, J., Lu, Y.L., 2017. Thermochemical storage performances of methane reforming with carbon dioxide in tubular and semi-cavity reactors heated by a solar dish system. Appl. Energy 185, 1994–2004.
- Yuan, F., Li, M.J., Ma, Z., Jin, B., Liu, Z.B., 2018. Experimental study on thermal performance of high-temperature molten salt cascaded latent heat thermal energy storage system. Int. J. Heat Mass Tran. 118, 997–1011.
- Yuan, F., Li, M.J., Qiu, Y., Ma, Z., Li, M.J., 2019. Specific heat capacity improvement of molten salt for solar energy applications using charged single-walled carbon nanotubes. Appl. Energy 250, 1481–1490.
- Zhang, M., Hong, Y., Ding, S., Hu, J., Fan, Y., Voevodin, A.A., Su, M., 2010. Encapsulated nano-heat-sinks for thermal management of heterogeneous chemical reactions. Nanoscale 2 (12), 2790–2797.
- Zhang, X., Liu, C., Rao, Z., 2018. Experimental investigation on thermal management performance of electric vehicle power battery using composite phase change material. J. Clean. Prod. 201, 916–924.
- Zhao, J.T., Lv, P.Z., Rao, Z.H., 2017. Experimental study on the thermal management performance of phase change material coupled with heat pipe for cylindrical power battery pack. Exp. Therm. Fluid Sci. 82, 182–188.
- Zhao, Y.W., Zhang, Y.D., Li, W.J., Hao, Y., Jin, H.G., 2018. Experimental investigation and thermodynamic analysis of effective hydrogen production driven by midand low-temperature solar heat. J. Clean. Prod. 176, 758–769.
- Zheng, Z.J., He, Y. He, Y.L., Wang, K., 2015. Numerical optimization of catalyst configurations in a solar parabolic trough receiver-reactor with non-uniform heat flux. Sol. Energy 122, 113–125.
- Zheng, Z.J., Xu, Y., 2018. A novel system for high-purity hydrogen production based on solar thermal cracking of methane and liquid-metal technology: thermodynamic analysis. Energy Convers. Manag. 157, 562–574.
- Zuo, H.Y., Liu, G.L., E, J.Q., Zuo, W., Wei, K.X., Hu, W.Y., Tan, J.Q., Zhong, D.Q., 2019. Catastrophic analysis on the stability of a large dish solar thermal power generation system with wind-induced vibration. Sol. Energy 183, 40–49.